DEVELOPMENT OF HETEROGENEOUS BASE CATAYST FOR TRANSESTERIFICATION REACTION

SHARMILLA ARUMUGAM

A thesis submitted in fulfillment of the requirements for the award of the Degree of Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
University Malaysia Pahang

NOV 2010

ABSTRACT

In this study of heterogeneous base catalyst of potassium nitrate with alumina support was investigated for transesterification of vegetable oil which is palm oil to methyl ester. The environmental problem could be overcome by using heterogeneous base catalyst because the separation of catalyst from final product is easier without use of any solvent and the catalyst is recyclable. The objective of this study is to characterise the developed heterogeneous base catalyst and test it in transesterification reaction at different operating parameters such as molar ratio of methanol to oil, reaction temperature and catalyst loading. After loading potassium nitrate of 35 wt.% on alumina followed by calcination at 773K for 5 h, the catalyst gave the highest basicity and the best catalytic activity for this reaction. The catalysts were characterized by using Fourier Transform Infrared Spectrometers (FTIR) and Scanning Electron Microscopy (SEM). It was found that KNO_3/ Al_2O_3 show high activity which converting 78.44% of palm oil to methyl ester with the optimum conditions which are at temperature 65°C, methanol to oil ratio of 15:1 and catalyst loading of 8.5% . Therefore, base heterogeneous catalyst of potassium on alumina of support has the potential to be used in biodiesel production processes due to its high activity on transesterification of palm oil.

ABSTRAK

Dalam kajian pemangkin alkali heterogen, nitrat kalium dengan alumina diselidiki untuk pengtransesteran minyak kelapa sawit kepada biodiesel. Masalah persekitaran dapat diatasi dengan menggunakan pemangkin alkali heterogen kerana pemisahan pemangkin dari produk lebih mudah tanpa menggunakan pelarut dan pemangkin ini dapat dikitar semula. Tujuan dari penelitian ini adalah untuk mengkarakterisasi pemangkin alkali untuk mengujinya dalam pengtransesteran pada parameter operasi yang berbeza seperti nisbah molar methanol terhadap minyak, reaksi suhu dan loading pemangkin. Apabila menggunakan sebanyak 35% nitrat kalium /alumina dan diikuti dengan kalsinasi pada 773K selama 5 jam, pemangkin memberikan kebesan tertinggi dan menunjukkan pemangkin terbaik untuk tindak balas ini. pemangkin ini dikaji dengan menggunakan Transformasi Fourier Spektrometer (FTIR) dan Mikroskop Elektron (SEM). KNO_3/ Al_2O_3 menunjukkan aktiviti tertinggi; iaitu ia dapat biodiesel sebanyak 78,44% dari minyak sawit dengan keadaan optimum yang pada suhu 65 ° C, metanol terhadap minyak 15:1 dan loading pemangkin 8.5%. Oleh kerana itu, pemangkin heterogen iaitu KNO_3/alumina munjukkan ia mempunyai berpotensi untuk menggunakan dalam pengeluaran biodiesel kerana dapat hasilkan banyak biodiesel.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABREAVIATION

IICA	-	Inter-American Institute for Cooperation on Agriculture
PME	-	Palm oil methyl ester
WCO	-	Waste Cooking Oil
FFA	-	Free Fatty Acid
BSP	-	Biomass Support Particles
FTIR	-	Fourier transform Infrared Spectrometer
GC	-	Gas Chromatography

LIST OF SYMBOLS

T	-	Temperature
°C	-	Degree Celcius
Ml	-	Mililiter
Min	-	Minute
K	-	Kelvin
w/w	-	Weight per weight
kg	-	Kilogram
g	-	Gram
%	-	Percentage
Rpm	-	Revolutions per minute
M	-	Molar (mol/dm3)
FFA	-	Free Fatty Acid

LIST OF APPENDICES

CHAPTER 1.0

INTRODUCTION

The recent increases in crude oil prices have created unprecedented opportunities to displace petroleum-derived materials with biodiesel. Biodiesel, as an alternative fuel, has many merits and made from renewable biological sources such as vegetable oils and animal fats. It is biodegradable and nontoxic has low emission profiles and so is environmentally beneficial. Apart from that, biodiesel is a renewable fuel, helping to achieve the European Union (EU) renewable energy target of 12% of total energy output to consist of renewable energy by 2010 (European Commission, 1997). Carbon dioxide produced by combustion of biodiesel can be recycled by photosynthesis, thereby minimizing the impact of biodiesel combustion on the greenhouse effect (Keorbitz, 1999; Agarwal and Das, 2001). Additionally biodiesel has a relatively high flash point (150 °C), which makes it less volatile and safer to transport or handle than petroleum diesel (Krawczyk, 1996).

In support of this increasing consumption there have been substantial increases in biodiesel production in recent years, a trend that is expected to continue. The EIA (Energy Information Administration) foreseeable that demand for biodiesel will be at least 6.5 million gallons in 2010 and 7.3 million gallons in 2020. Based on biodiesel's potential as a lubricity additive, demand could reach as much as 470 million gallons in 2010 and 630 million gallons in 2020. Now the major producer of biodiesel in the world is Germany. It has produced 2539 million ton in 2009 whilst Malaysia nearly exported 76 million gallons of biodiesel in 2009. So far 91 biodiesel licences issued to date, 15 plants with a combined 1.6 million tonnes capacity have been built. The plant in Johor have a capacity to produce 180 000 tonnes of biodiesel per year.

A mixture with 10% vegetable oil has been used in pre-combustion chamber engines to maintain total power without any alterations or adjustments to the engine in Brazil. At that point, it was not practical to substitute 100% vegetable oil for diesel fuel, but a blend of 20% vegetable oil and 80% diesel fuel was successful. Some short-term experiments used up to a 50/50 ratio also provide good solution for well maintain engine (Fangrui et al., Ma, 1998).

1.1 Background of Study

A renewable diesel fuel that is produced from fats and oils is known as biodiesel. It consists of the simple alkyl esters of fatty acids, most typically the methyl esters. It environmentally benign substitute instead of petroleum based fuels (Zabeti et al., 2009). The biodiesel would reduce emissions of CO, $SO_{X,}$ unburned hydrocarbons and particulate matter during the combustion process. So it is very advantageous in environmentally sensitive areas such as large cities and mines. Moreover, it is biodegradable, non-toxic, and better lubricity (Demirbas et al., 2008). The demand of biodiesel is very high now these days due to the increase in number of population and environmental concern.

Transesterification is crucial reaction that takes place during convert the vegetable oil to biodiesel which is with alcohol to form esters and glycerol. Excess alcohol has been used to shift the equilibrium to the products since the reaction is reversible (Helwani et al., 2009). Only simple alcohol can be used for transesterification process such as methanol, ethanol, propanol and amyl alcohol. However, methanol is most selective choice in industries due to its chemical and physical nature such as shortest alcohol chain and polar.

Many researchers have been introduced heterogeneous catalyst as magnificent catalyst for their experiment. Example of heterogeneous catalyst commercially used are CaO, SrO, BaO, and $Ca(OCH_3)_2$. Homogeneous catalyst has been widely used in industries such are KOH, NaOH, and CH_3ONa (Liu et al., 2007). Alkali metal hydroxides or alkoxides can be used as transesterification catalysts. Hydroxides are cheaper than alkoxides, but must be used in higher concentrations to achieve good reaction (Freedman et al., 1984). Particulate heterogeneous catalysts can be readily separated from products following reaction allowing the catalyst to be reused, generating less waste, and consuming less energy. Recycling and reactivating the catalyst have been studied and found to maintain efficiency for use in industrials.

1.2 Problem Statement

Due to the fact that the supply of fossil fuel is limited while energy demand continues rise, biodiesel has been introduced as alternative renewable energy. The International Energy Outlook, an annual forecast by the U.S. Energy Information Administration forecast due to the driven by population and economic growth in developing countries, the world in 2035 would be more dependent on fossil fuels than ever, it finds. Countries overall would be consuming 49 percent more energy and spewing 43 percent more carbon dioxide into the atmosphere in 2035 than in 2007. To get rid from this problem, biodiesel plays essential role in manner to reduce the emissions of carbon dioxide and reduce the consumption fossil fuel.

The employment of homogeneous catalyst in the production of biodiesel has brought several disadvantages. Since homogeneous catalyst can be dissolved in the methanol; the separation of catalyst from the product is difficult. Therefore, the catalyst recycling may be more costly and challenging. Thus, the manufacturing cost increases. Other disadvantage of homogeneous base catalyst is soap formation which could reduce the catalytic efficiency.

Considering the disadvantageous of the homogeneous catalyst, vegetable oil transesterification using heterogeneous catalyst, potassium nitrate with alumina has been studied in the present research.

1.3 Research Objectives

1. To synthesize and characterize potassium nitrate with alumina
2. To identify the optimum operating condition for the reaction

1.4 Scope of Study

This study was carried out by using palm oil with Al_2O_3/KNO_3 as base heterogeneous catalyst for the tansesterification reaction. In this study three parameters have been investigated which are temperature, molar ratio of alcohol to oil, and catalyst ratio.

The range of studying for operating are:-

1. Temperature : 35°C - 65°C
2. Mass ratio of catalyst to oil : 4.5% - 9.5%
3. Molar ratio of methanol to oil : 15:1 to 18:1

1.5 Rationale & Significance

The contributions of the present research are:

a) It could overcome environmental issue such as reduce global warming gas emission and displace imported petroleum. Besides that the catalyst could be easily recycled.

b) The cost of manufacturing will be reduced due to the simple process which is the purification process.

CHAPTER 2.0

LITERATURE REVIEW

2.1 Biodiesel

With the exception of electricity and nuclear energy, the majority of the worlds energy needs are supplied through petrochemical sources, coal and natural gas. All these sources are finite and at current usage rates will be consumed by the end of the next century (C. Sookman et al., 1999). The depletion of world petroleum reserves and increased environmental concerns has stimulated recent interest in alternative sources for petroleum-based fuels. Biodiesel has arisen as a potential candidate for a diesel substitute due to the similarities it has with the petroleum-based diesel.

The use of vegetable oils as alternative fuel has been around since 1990 when the inventor of the diesel engine Rudolph Diesel first tested them, in his compression engine (Foglia, Jones,Haas, & Scott, 2000). Biodiesel also has been known as oxygenated fuel, meaning that it emit low amount of carbon to the environment because it's contain higher hydrogen and oxygen than carbon (Armas et al., 2008).

Furthermore, the sulphur contents of vegetal oils are close to zero and consequently, the environmental damage caused by sulphuric acid is reduced (Vicente et al., 1998)

2.1.1 Raw material

Basically biodiesel have been produced by using vegetable oil and animal fats. But commonly biodiesel derived from vegetable oil.

2.1.2 Animal fat

Apart from the vegetable oils, it is worth mentioning the possibility of producing biodiesel from animal fats which is an interesting option for the meat packing industries, by increasing the value of usefulness of marginal by products like tallow (Noordam and Withers, 1996). The potential of biodiesel production, from bovine cattle only taken into account, 64 million animals were slaughtered in 2007 in South Africa, where Brazil, Argentina and Uruguay are particularly highlighted. According to estimations of IICA- Paraguay (Souto 2008), if 50% of the production of bovine tallow from slaughtering, there would be a volume of about 9.5 million litres of biodiesel annually, enough quantity to complete the 1% established blend (Federico Ganduglia, 2002). One of the studies was investigated of transesterification on animal fat. At the end of these experiments, the maximum yield of 89% was obtained in two steps which is 0.35 (w/w) methanol/fat was used at reaction temperature of 62 °C for 2 h reaction period and by catalysing with 0.08 (w/w) H_2SO_4/fat and 0.01 (w/w) NaOH/fat ratios (Atilla Koca et al., 2009).

2.1.3 Vegetable oil

Vegetable oil has been used widely in the industrial to produce biodiesel. It gives more efficient of product which is biodiesel than animal fats. Different countries are looking for different types of vegetable oils as substitutes for diesel fuels. Generally, the most abundant vegetable oil in a particular region is the most common feedstock. Thus, rapeseed and sunflower oils are predominantly used in Europe; soybeans are commonly used in the United States for food products which has led to soybean biodiesel becoming the primary source for biodiesel in this country. In India, jatropha oil is used as a significant fuel source, palm oil in the South-East Asia (mainly Malaysia and Indonesia) and coconut oil are being considered in the Philippines (Barnwal and Sharma, 2005; Demirbas, 2007). The worldwide consumption of soybean oil is this highest in 2003 which about 27.9 million metric tonnes and followed by palm oil with 27.8 million metric tonnes of worldwide consumption. The table 2.1 shows that the different fatty acid in their own oil.

Table 2.1: The composition of fatty acids in vegetables oil (Jackson et al., 2006)

Fatty acid	Soybean	Cottonseed	Palm	Coconut oil
Lauric	0.1	0.1	0.1	46.5
Myristic	0.1	0.7	1.0	19.2
Palmitic	10.2	20.1	42.8	9.8
Stearic	3.7	2.6	4.5	3.0
Oleic	22.8	19.2	40.5	6.9
Linoleic	53.7	55.2	10.1	2.2
Linolenic	8.6	0.6	0.2	0.0

2.2.2.1 Palm oil as biodiesel feedstock

Palm oil biodiesel is produced from the edible vegetable oil obtained from the fruit of the oil palm tree. Biodiesel from palm oil are taking on renewed global importance as countries seek to substitute the soaring price of conventional oil and also cut hazardous emissions. Palm oil methyl ester (PME), differs from other types of biodiesel in its grade of molecule unsaturation, this is because each type of oil contain different amount of fatty acid and properties. Table 2.2 shows the properties of palm oil.

Table 2.2: The physical properties of palm oil

Physical state and appearance	Liquid
Molecular weight (g/mol)	846.1
Colour	Light yellow
Viscosity	57.85 @ 30°C
Heat Capacity KJ/kg-C	1.875 @ 30°C
Conductivity W/m-C	0.1717
Density kg/m3	885
Flash points (°C)	162

2.2.2.2 Waste cooking oil

The increasing production of waste cooking oils (WCOs) from household and industrial sources is a growing problem in all around the world. Waste edible oils and fats pose significant disposal problems in many parts of the world and resulting problems for wastewater treatments plants and energy loss, or are integrated into the food chain through animal feeding, thus becoming a potential cause of human health problems (Felizardo et al., 2006). So in the past much of this waste cooking oil have been used in the production of biodiesel (Kulkarni and Dalai, 2006). Compared to petroleum-based diesel, the high cost of biodiesel is a major barrier to its commercialization. It costs approximately one and a half times that of petroleum-based diesel depending on feedstock oils (Prokop, 2002; Lott, 2002). It is reported that approximately 70–95% of the total biodiesel production cost arises from the cost of raw material; that is, vegetable oil or animal fats (Krawczyk, 1996; Connemann and Fischer, 1998). Therefore, the use of waste cooking oil should greatly reduce the cost of biodiesel because waste oil is available at a relatively low price.

Based on estimates from seven countries, a total of about 0.4 Mt is collected within the EU, mainly from the catering industry, while the amount that could be collected is estimated to be considerably higher, possibly from 0.7 to 1 Mt. Its price is variable, but in general is approximately half that of virgin oil (Gomez et al., 2002).

One of the paper review revealed that biodiesel could be produced from waste cooking oil via two-step catalyzed process. First, free fatty acid (FFA) of the WCO with an acid value of 66.40 was esterified with methanol catalyzed by polyferric sulfate (PFS). Second, the esterified WCO was transesterified with methanol catalyzed by potassium hydroxide to produce crude biodiesel. The crude biodiesel was purified by molecular distillation to produce purified biodiesel (fatty acid methyl ester, FAME). The highest yield of FAME by molecular distillation from the crude biodiesel was 98.32% ± 0.17% at an evaporator temperature of 120 °C (Shuze Tang et al., 2010).

Other than that, another study investigated production biodiesel from waste cooking oil via acid catalysed. Albeit, the acid catalysed cause slow reaction, but it has been suggested best way to produce efficient biodiesel (Freedman et al. 1984). The most advantage of producing biodiesel via acid catalysed rather than base catalysed is it prevents form soap. Soap formation reduces catalyst efficiency, causes an increase in viscosity, leads to gel formation and makes the separation of glycerol difficult (Guo and Leung, 2003). The reaction conditions were set to a 50:1 molar ratio of methanol to oil, a 1.3:1 molar ratio of sulphuric acid to waste oil, a reaction temperature of 80 °C and a pressure of 400 kPa (M. Kates et al,. 2003).

2.2 Process

There are some feasible process could solve the problem which to reduce viscosity in the virgin oil. The eminent process that most of industries prefer is transesterification which is most easy and economical. Whilst, other process could be used are direct use and blend, micro emulsion, thermal cracking and with critical methanol.

2.2.1 Direct use and blend

The direct use of vegetable oils in diesel engines is problematic and has many inherent failings due to its high viscosity. Although some diesel engines can run pure vegetable oils engine, turbocharged direct injection engines such as trucks are prone to many problems (BTCE, 1994). The term use ratio of 1:10 to 1:20 oil to diesel has been found successful (Ma, 1999). According to the study of (Ma, 1999), the canola oil and diesel are very similar except the viscosity. Viscosity of canola is six times than diesel, it creates such a huge problem with flow of oil from fuel tank to the engine, blockages in filters, and subsequent engine power losses. Further, engines can suffer coking and gumming which leads to sticking of piston rings due to multi bonded compounds undergoing pyrolysis (Ma, 1999).